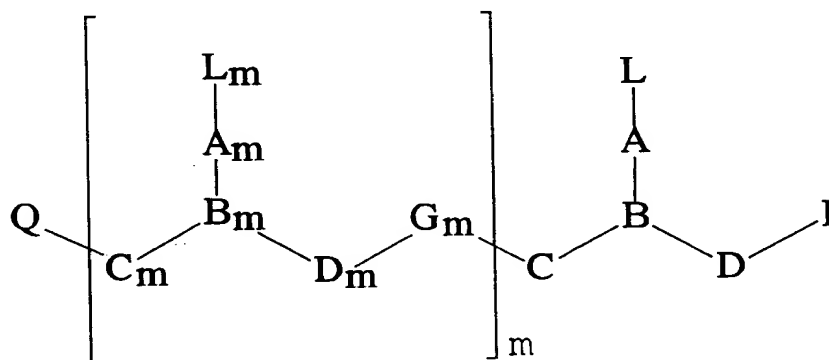


## WHAT IS CLAIMED IS:

1. A peptide nucleic acid conjugate comprising:  
a peptide nucleic acid;  
said peptide nucleic acid having a backbone;  
5 said backbone having an amino end, a carboxyl end, and  
a plurality of amino groups;  
said amino groups each having a tethered nucleobase;  
and a conjugate bound to said peptide nucleic acid either  
directly or through a linking moiety.
- 10 2. A peptide nucleic acid conjugate of claim 1  
wherein said conjugate is bound through said linking moiety  
to at least one of said backbone, said tether, or said  
nucleobase.
- 15 3. A peptide nucleic acid conjugate of claim 1  
wherein said conjugate is bound to said backbone.
4. A peptide nucleic acid conjugate of claim 3  
wherein said conjugate is bound to at least one of said  
amino end or said carboxyl end of said backbone.
- 20 5. A peptide nucleic acid conjugate of claim 1  
wherein said conjugate is bound to said nucleobase or said  
tether.

6. A peptide nucleic acid conjugate of claim 1  
 wherein said conjugate is a reporter enzyme, a reporter  
 molecule, a steroid, a carbohydrate, a terpene, a peptide, a  
 protein, an aromatic lipophilic molecule, a non aromatic  
 5 lipophilic molecule, a phospholipid, an intercalator, a cell  
 receptor binding molecule, a crosslinking agent, a water  
 soluble vitamin, a lipid soluble vitamin, an RNA/DNA  
 cleaving complex, a metal chelator, a porphyrin, an  
 alkylator, or a polymeric compound selected from polymeric  
 10 amines, polymeric glycols and polyethers.

A peptide nucleic acid conjugate of the formula:



wherein:

B

m is an <sup>integer</sup> ~~integer~~ from 1 to about 50;

L and L<sub>m</sub> independently are R<sup>12</sup>(R<sup>13</sup>)<sub>a</sub>; wherein:

15

R<sup>12</sup> is hydrogen, hydroxy, (C<sub>1</sub>-C<sub>4</sub>)alkanoyl, a

naturally occurring nucleobase, a non-naturally occurring nucleobase, an aromatic moiety, a DNA intercalator, a nucleobase-binding group, a heterocyclic moiety, a reporter ligand, or a conjugate;

provided that at least one of  $R^{12}$  is a naturally occurring nucleobase, a non-naturally occurring nucleobase, a DNA intercalator, or a nucleobase-binding group;

$R^{13}$  is a conjugate; and

$a$  is 0 or 1;

$C$  and  $C_m$  independently are  $(CR^6R^7)_y$ ; wherein:

$R^6$  and  $R^7$  independently are hydrogen, a side chain of a naturally occurring alpha amino acid,  $(C_2-C_6)$  alkyl, aryl, aralkyl, heteroaryl, hydroxy,  $(C_1-C_6)$  alkoxy,  $(C_1-C_6)$  alkylthio, a conjugate,  $NR^3R^4$ ,  $SR^5$  or  $R^6$  and  $R^7$  taken together complete an alicyclic or heterocyclic system;

wherein  $R^5$  is hydrogen, a conjugate,  $(C_1-C_6)$  alkyl, hydroxy-, alkoxy-, or alkylthio-substituted  $(C_1-C_6)$  alkyl; and

$R^3$  and  $R^4$  independently are hydrogen, a conjugate,  $(C_1-C_4)$  alkyl, hydroxy- or alkoxy- or alkylthio-substituted  $(C_1-C_4)$  alkyl, hydroxy, alkoxy, alkylthio or amino;

$D$  and  $D_m$  independently are  $(CR^6R^7)_z$ ;

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each of y and z is zero or an integer from 1 to 10,  
wherein the sum y + z is greater than 2 but not more than  
10;

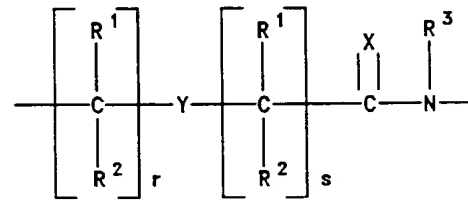
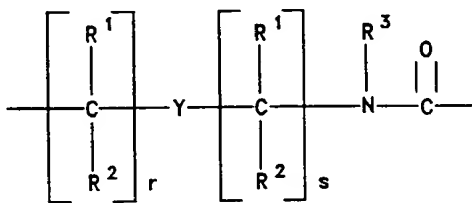
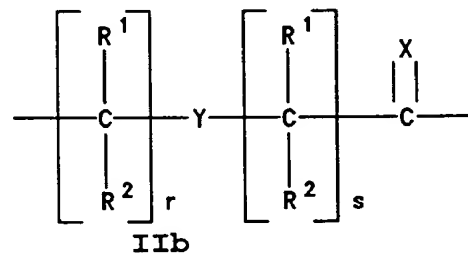
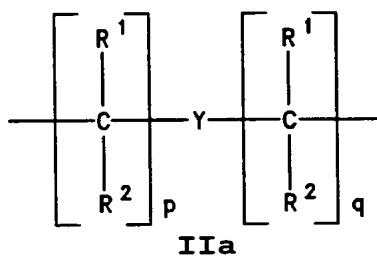
$G_m$  is independently  $-NR^3CO-$ ,  $-NR^3CS-$ ,  $-NR^3SO-$ , or  
5  $-NR^3SO_2-$  in either orientation;

each pair of  $A-A_m$  and  $B-B_m$  are selected such that:

(a) A or  $A_m$  is a group of formula (IIa), (IIb) or  
(IIc) and B or  $B_m$  is N or  $R^3N^+$ ; or

(b) A or  $A_m$  is a group of formula (IIc) and B or  $B_m$  is

10 CH;



IIc

IIId

wherein:

X is O, S, Se,  $\text{NR}^3$ ,  $\text{CH}_2$  or  $\text{C}(\text{CH}_3)_2$ ;

Y is a single bond, O, S or  $\text{NR}^4$ ;

each of p and q is zero or an integer from 1 to 5, ~~the~~  
5 ~~sum p+q being not more than 10;~~

each of r and s is zero or an integer from 1 to 5, ~~the~~  
~~sum r+s being not more than 10;~~

$\text{R}^1$  and  $\text{R}^2$  independently are hydrogen,  $(\text{C}_1\text{-C}_4)$ alkyl,  
hydroxy-substituted  $(\text{C}_1\text{-C}_4)$ alkyl, alkoxy-substituted  $(\text{C}_1\text{-C}_4)$ alkyl, alkylthio-substituted  $(\text{C}_1\text{-C}_4)$ alkyl, hydroxy,  
10 alkoxy, alkylthio, amino, halogen or a conjugate;

I is  $-\text{NR}^8\text{R}^9$  or  $-\text{NR}^{10}\text{C}(\text{O})\text{R}^{11}$ ; wherein:

$\text{R}^8$ ,  $\text{R}^9$ ,  $\text{R}^{10}$  and  $\text{R}^{11}$  independently are hydrogen,  
alkyl, an amino protecting group, a reporter  
15 ligand, an intercalator, a chelator, a peptide, a  
protein, a carbohydrate, a lipid, a steroid, a  
nucleoside, a nucleotide, a nucleotide  
diphosphate, a nucleotide triphosphate, an  
oligonucleotide, an oligonucleoside, a soluble  
20 polymer, a non-soluble polymer or a conjugate;

Q is  $-\text{CO}_2\text{H}$ ,  $-\text{CO}_2\text{R}^8$ ,  $-\text{CO}_2\text{R}^9$ ,  $-\text{CONR}^8\text{R}^9$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{SO}_2\text{NR}^{10}\text{R}^{11}$  or  
an activated derivative of  $-\text{CO}_2\text{H}$  or  $-\text{SO}_3\text{H}$ ; and

wherein at least one of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{R}^8$ ,  
 $\text{R}^9$ ,  $\text{R}^{10}$ ,  $\text{R}^{11}$ ,  $\text{R}^{12}$  and  $\text{R}^{13}$  is a conjugate wherein said conjugate  
25 is a reporter enzyme, a reporter molecule, a steroid, a

carbohydrate, a terpene, a peptide, a protein, an aromatic lipophilic molecule, a non aromatic lipophilic molecule, a phospholipid, an intercalator, a cell receptor binding molecule, a crosslinking agent, a water soluble vitamin, a lipid soluble vitamin, an RNA/DNA cleaving complex, a metal chelator, a porphyrin an alkylator, or a polymeric compound selected from polymeric amines, a polymeric glycols and polyethers; and

wherein said conjugate optionally includes a linking moiety.

8. A peptide nucleic acid conjugate of claim 1 wherein said conjugate includes a linking moiety.

9. A peptide nucleic acid conjugate of claim 1 wherein at least one group  $R^{12}$  is a conjugate.

10. A peptide nucleic acid conjugate of claim 1 wherein at least one group  $R^{13}$  is a conjugate.

11. A peptide nucleic acid conjugate of claim 1 wherein at least one of  $R^1$ ,  $R^2$  or  $R^3$  is a conjugate.

12. A peptide nucleic acid conjugate of claim 1 wherein at least one of said A-A<sub>m</sub> groups include at least one of  $R^1$ ,  $R^2$ , and  $R^3$ .

~~13~~<sup>7</sup>. A peptide nucleic acid conjugate of claim ~~11~~<sup>5</sup>  
wherein at least one of said B-B<sub>m</sub> groups or said G-G<sub>m</sub> groups  
include at least one group R<sup>3</sup>.

~~14~~<sup>8</sup>. A peptide nucleic acid conjugate of claim ~~11~~<sup>1</sup>  
5 wherein at least one of R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup> and R<sup>11</sup> is a conjugate.

~~15~~<sup>9</sup>. A peptide nucleic acid conjugate of claim ~~14~~<sup>8</sup>  
wherein at least one of said groups Q or I include at least  
one of groups R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup> and R<sup>11</sup>.

~~16~~<sup>10</sup>. A peptide nucleic acid conjugate of claim ~~15~~<sup>1</sup>  
10 wherein at least one of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> is a conjugate.

~~17~~<sup>11</sup>. A peptide nucleic acid conjugate of claim ~~16~~<sup>10</sup>  
wherein at least one of said groups D-D<sub>m</sub>, or C-C<sub>m</sub> include at  
least one of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup>.

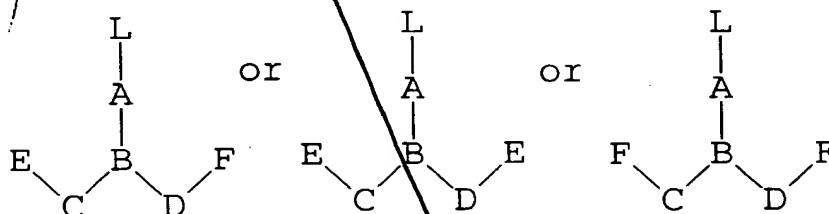
~~18~~<sup>12</sup>. A peptide nucleic acid conjugate of claim ~~17~~<sup>1</sup>  
15 wherein m is from 1 to about 200.

~~19~~<sup>13</sup>. A peptide nucleic acid conjugate of claim ~~18~~<sup>1</sup>  
wherein m is from 1 to about 50.

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14  
20. A peptide nucleic acid conjugate of claim 1  
wherein m is from 1 to about 20.

21. A compound having one of the following formulas:



wherein:

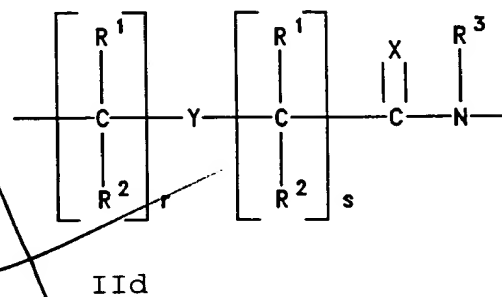
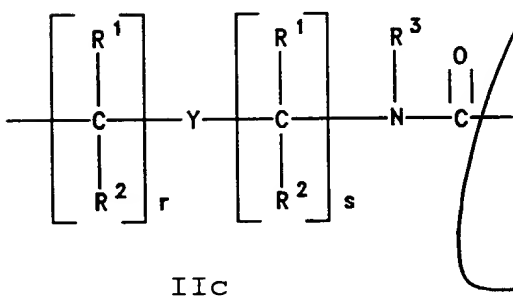
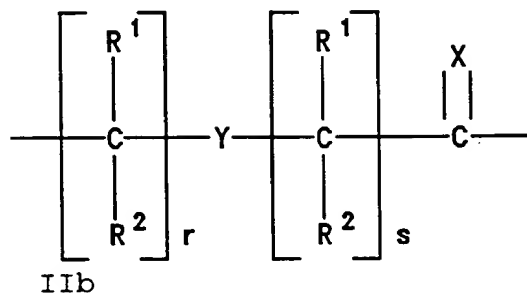
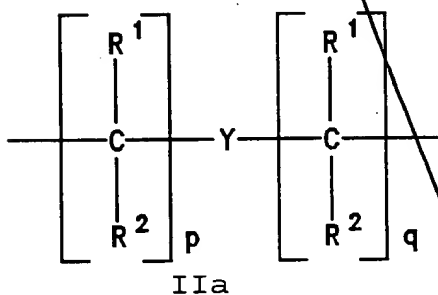
5 L is  $R^{12}(R^{13})_a$ ; wherein:

$R^{12}$  is hydrogen, hydroxy,  $(C_1-C_4)$ alkanoyl, a naturally occurring nucleobase, a non-naturally occurring nucleobase, an aromatic moiety, a DNA intercalator, a nucleobase-binding group, a heterocyclic moiety, a reporter ligand, or a conjugate and at least one of  $R^{12}$  is a naturally occurring nucleobase, a non-naturally occurring nucleobase, a DNA intercalator, or a nucleobase-binding group;

10  
15  $R^{13}$  is a conjugate; and  
a is 0 or 1;

A and B are selected such that:

- (a) A is a group of formula (IIa), (IIb) or (IIc) and B is N or  $R^3N^+$ ; or  
 (b) A is a group of formula (IIId) and B is CH;



5 where:

X is O, S, Se,  $NR^3$ ,  $CH_2$  or  $C(CH_3)_2$ ;

Y is a single bond, O, S or  $NR^4$ ;

p and q independently are zero or an integer from 1 to 5, ~~the sum p+q being not more than 10;~~

10 r and s independently are zero or an integer from 1 to 5, ~~the sum r+s being not more than 10;~~

~~the sum r+s being not more than 10;~~

$R^1$  and  $R^2$  independently are hydrogen,  $(C_1-C_4)$ alkyl,

hydroxy-substituted (C<sub>1</sub>-C<sub>4</sub>)alkyl, alkoxy-substituted (C<sub>1</sub>-C<sub>4</sub>)alkyl, alkylthio-substituted (C<sub>1</sub>-C<sub>4</sub>)alkyl, hydroxy, alkoxy, alkylthio, amino, halogen or a conjugate;

$C$  is  $(CR^6R^7)_y$ ;

5 D is  $(CR^6R^7)_z$ ; wherein:

R<sup>6</sup> and R<sup>7</sup> independently are hydrogen, a side chain of a naturally occurring alpha amino acid, (C<sub>2</sub>-C<sub>6</sub>) alkyl, aryl, aralkyl, heteroaryl, hydroxy, (C<sub>1</sub>-C<sub>6</sub>) alkoxy, (C<sub>1</sub>-C<sub>6</sub>) alkylthio, a conjugate, NR<sup>3</sup>R<sup>4</sup> and SR<sup>5</sup> or R<sup>6</sup> and R<sup>7</sup> taken together complete an alicyclic or heterocyclic system;

15 R<sup>3</sup> and R<sup>4</sup> independently are hydrogen, a conjugate,  
(C<sub>1</sub>-C<sub>4</sub>)alkyl, hydroxy- or alkoxy- or alkylthio-  
substituted (C<sub>1</sub>-C<sub>4</sub>)alkyl, hydroxy, alkoxy,  
alkylthio or amino; and

R<sup>5</sup> is hydrogen, a conjugate, (C<sub>1</sub>-C<sub>6</sub>)alkyl, hydroxy-, alkoxy-, or alkylthio- substituted (C<sub>1</sub>-C<sub>6</sub>)alkyl;

each of  $y$  and  $z$  is zero or an integer from 1 to 10, the sum  $y + z$  being greater than 2 but not more than 10;

20 E independently is COOH, CSOH, SOOH, SO<sub>2</sub>OH or an  
activated or protected derivative thereof;

F independently is  $\text{NHR}^3$  or  $\text{NPgR}^3$ , where Pg is an amino protecting group; and

at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>12</sup>, and R<sup>13</sup> is  
25 a conjugate wherein said conjugate is a reporter enzyme, a  
reporter molecule, a steroid, a carbohydrate, a terpene, a  
peptide, a protein, an aromatic lipophilic molecule, a non  
aromatic lipophilic molecule, a phospholipid, an  
intercalator, a cell receptor binding molecule, a  
30 crosslinking agent, a water soluble vitamin, a lipid soluble  
vitamin, an RNA/DNA cleaving complex, a metal chelator, a  
porphyrin an alkylator, or a polymeric compound selected  
from polymeric amines, polymeric glycols and polyethers;  
and wherein said conjugate optionally includes a linking  
35 moiety.

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16  
22. A peptide nucleic acid conjugate of claim 21  
wherein said conjugate includes a linking moiety.

17  
23. A peptide nucleic acid conjugate of claim 21  
wherein  $R^{12}$  is a conjugate.

5 24. A peptide nucleic acid conjugate of claim 21  
wherein  $R^{13}$  is a conjugate.

18  
25. A peptide nucleic acid conjugate of claim 21  
wherein at least one group  $R^3$  is a conjugate.

19  
26. A peptide nucleic acid conjugate of claim 21  
10 wherein at least one of said groups A or said groups B  
include a conjugate.

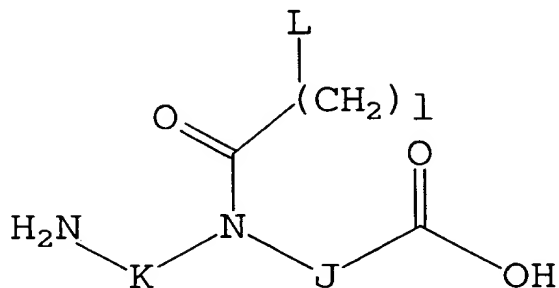
20  
27. A peptide nucleic acid conjugate of claim 21  
wherein at least one of group  $R^1$  or group  $R^2$  is a conjugate.

21  
28. A peptide nucleic acid conjugate of claim 21  
15 wherein at least one of  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ , and  $R^7$  is a conjugate.

22  
29. A peptide nucleic acid conjugate of claim 21  
wherein at least one of said groups C or said groups D  
include a conjugate.

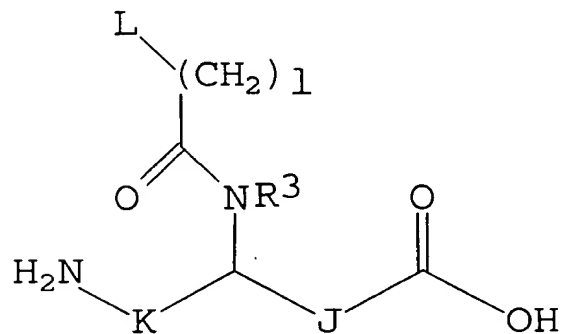
23

30/ A peptide nucleic acid conjugate comprising a plurality of PNA monomers wherein at least one of said PNA monomers has the formula:

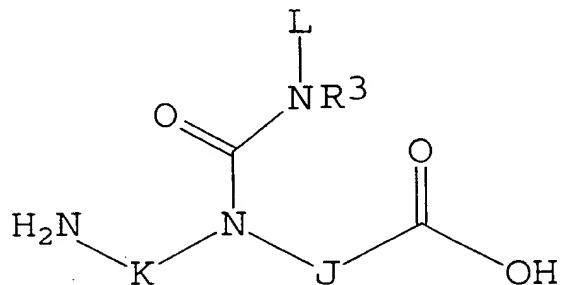


or formula:

5



or formula:



233

08817067 040497  
164070 20070800

12330

wherein:

L is  $R^{12}(R^{13})_a$ ; wherein:

$R^{12}$  is hydrogen, hydroxy,  $(C_1-C_4)$ alkanoyl, a naturally occurring nucleobase, a non-naturally occurring nucleobase, an aromatic moiety, a DNA intercalator, a nucleobase-binding group, a heterocyclic moiety, a reporter ligand, or a conjugate and at least one of  $R^{12}$  is a naturally occurring nucleobase, a non-naturally occurring nucleobase, a DNA intercalator, or a nucleobase-binding group;

$R^{13}$  is a conjugate; and

a is 0 or 1;

K is  $(CR^6R^7)_z$ ;

J is  $(CR^6R^7)_y$ ; wherein:

$R^6$  and  $R^7$  are independently hydrogen, a side chain of a naturally occurring alpha amino acid,  $(C_2-C_6)$  alkyl, aryl, aralkyl, heteroaryl, hydroxy,  $(C_1-C_6)$  alkoxy,  $(C_1-C_6)$  alkylthio, a conjugate,  $NR^3R^4$  and  $SR^5$  or  $R^6$  and  $R^7$  taken together complete an alicyclic or heterocyclic system;

$R^3$  and  $R^4$  independently are hydrogen, a conjugate,  $(C_1-C_4)$ alkyl, hydroxy- or alkoxy- or alkylthio-substituted  $(C_1-C_4)$ alkyl, hydroxy, alkoxy, alkylthio or amino;

$R^5$  is hydrogen, a conjugate,  $(C_1-C_6)$ alkyl, hydroxy-, alkoxy-, or alkylthio- substituted  $(C_1-C_6)$ alkyl;

each of y and z is zero or an integer from 1 to 10, the sum  $y + z$  being greater than 2 but not more than 10;

l is an integer from 1 to 5; and

at least one of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^{12}$ , and  $R^{13}$  is a conjugate wherein said conjugate is a reporter enzyme, a reporter molecule, a steroid, a carbohydrate, a terpene, a peptide, a protein, an aromatic lipophilic molecule, a non aromatic lipophilic molecule, a phospholipid, an

intercalator, a cell receptor binding molecule, a crosslinking agent, a water soluble vitamin, a lipid soluble vitamin, an RNA/DNA cleaving complex, a metal chelator, a porphyrin an alkylator, or a polymeric compound selected  
5 from polymeric amines, polymeric glycols and polyethers; and wherein said conjugate optionally includes a linking moiety.

<sup>24</sup>  
31. A peptide nucleic acid conjugate of claim <sup>23</sup>~~30~~  
wherein said conjugate includes a linking moiety.

<sup>25</sup>  
10 32. A peptide nucleic acid conjugate of claim <sup>23</sup>~~30~~  
wherein R<sup>12</sup> is a conjugate.

<sup>26</sup>  
33. A peptide nucleic acid conjugate of claim <sup>23</sup>~~30~~  
wherein R<sup>13</sup> is a conjugate.

<sup>27</sup>  
15 34. A peptide nucleic acid conjugate of claim <sup>23</sup>~~30~~  
wherein at least one of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> is a conjugate.

<sup>28</sup>  
35. A peptide nucleic acid conjugate of claim <sup>23</sup>~~30~~  
wherein at least one of said group K or said group J includes a conjugate.

<sup>29</sup>  
20 36. A peptide nucleic acid conjugate of claim <sup>23</sup>~~30~~  
wherein said group R<sup>3</sup> is a conjugate.

add  
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